

**SEMI-ANNUAL PROGRESS REPORT**

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SPACE ADMINISTRATION**

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**Rensselaer Polytechnic Institute  
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# Rensselaer Polytechnic Institute

## Semi-Annual Progress Report National Aeronautics and Space Administration Grant NsG-100-60 March 1, 1965 to August 31, 1965

### INTRODUCTION

Occupancy of the new Materials Research Center which was financed by a 1.5 million dollar grant from the National Aeronautics and Space Administration was completed during this report period and the research studies described in this report are, for the first time essentially housed under one roof. This should further enhance the interdisciplinary aspects of the program as well as enable more productive research.

Two new studies were initiated during this report period. They are Project No. 470.37 entitled "Electron Spin Resonance" and Project No. 470.38 entitled "Polymer Characterization." No projects were terminated during this time.

This ninth semi-annual report from the Interdisciplinary Materials Research program at Rensselaer follows the format established by previous reports. It contains a brief description of the studies that were carried out under each research project during the report period along with some interim results and a description of the studies that are planned for the ensuing six months.

### RESEARCH PROJECTS

#### Mechanical Properties of Polymers

470.05

#### Senior Investigator:

S.S. Sternstein, Ph.D.  
Associate Professor of Chemical  
Engineering

#### Research Staff:

L.C. Cessna, Ph.D.  
Research Associate  
R. Dujari, B.S.  
Graduate Assistant  
H. Gelwasser, B.Ch.E.  
Graduate Assistant  
G.M. Huffman, B.S.  
Graduate Fellow  
R.I. Schwartz, M.S.  
Graduate Assistant  
R. Watkins, B.S.  
Graduate Assistant

### A. Fracture of Polymers

Fracture data on glasslike polymers, under uniaxial creep and constant strain rate loading histories, have been shown to be in agreement with theoretical analysis of the fracture of viscoelastic media. Experimental and theoretical analysis of compound loading histories, e.g., cyclical stress superimposed upon a creep load, is now in progress. For this purpose, a special loading jig has been constructed. In addition, a theoretical analysis of the effect of a biaxial stress field on the viscoelastic behavior of the failure initiation site, in amorphous glasslike polymers, is being initiated. (Partially supported by the Institute of Paper Chemistry).

### B. Polymer Network Mechanics

The application of minimum free energy criteria, as developed by this project's senior investigator, to elastomeric networks is now in progress. It is the ultimate goal of this analysis to obtain constitutive equations for bulk polymers which are more generally applicable at high deformations and cross link densities than presently available theories permit. (Supported by the National Science Foundation).

Description of the mechanical response of composite plastics, e.g., a glasslike matrix with a rubberlike dispersed phase, in terms of this network theory is now being formulated. Application of the fracture concepts developed in this laboratory to such systems is also being considered.

### C. Viscoelastic Properties of Polymers

An apparatus to simultaneously measure the swelling and absorption phenomena of various solvents and polymers has been constructed. Periodic displacement of a solvent environment by mercury will allow volumetric changes, as a function of time, to be obtained for the attacked polymer. These data are of value in the thermodynamic analysis of solvent attack and also in the interpretation of degradation of mechanical properties by various solvents, as studied previously by torsion pendulum techniques. Dielectric and dynamic mechanical spectra studies on various polymers and copolymers are continuing.

### D. High Pressure Infrared Spectra

Analysis of spectral shifts of various high polymers at high pressures has indicated a need for unit cell dimensions at the same pressures. This study is being initiated and it is hoped that such data will lead to a complete picture of the deformation resistance of a high polymer to pressure loading.

A Study of the Interaction of Dislocation  
with the Discrete Second-Phase Particles  
in Dispersion-Strengthened Alloys

470.09

Senior Investigator:	G.S. Ansell, Ph.D. Professor of Metallurgical Engineering
Research Staff:	C.J. Barton, M. Met. E. Graduate Assistant N. Ramchandran, B.S. Graduate Assistant H.S. Kim, M. Met. E. Research Assistant D. Passoja, B.S. Graduate Assistant E. Brien Research Fellow

The objective of this program has been to delineate the effects associated with the presence of a distributed second-phase in a crystalline matrix by both theoretical considerations and experimental observations.

During this period, research efforts have centered principally upon experimental observations utilizing both replication and thin film transmission electron microscopy techniques. The specific areas investigated include:

A. Recovery and Recrystallization Kinetics in Two-Phase Systems

It has been well established that the presence of a distributed second-phase inhibits grain boundary migration, particularly secondary recrystallization in dispersion-strengthened alloy systems. Unfortunately, however, the mechanism by which this retardation occurs has never been delineated. Utilizing hot stage transmission electron microscopy and cine<sup>1</sup> sequence recording techniques, studies of the rate of substructural recovery of cold worked structures and the interaction of migrating grain boundaries with second-phase particles have been made. The alloy system investigated is the Al-Al<sub>2</sub>O<sub>3</sub> SAP-type alloy. This alloy has afforded direct observation of these kinetic processes without the concomitant change in distributed phase structure which usually accompanies these high temperature processes. In particular, the thermal effect on the cold worked structures can be described in terms of two distinctive mechanisms. At approximately 0.5 of the absolute melting temperature localized shifting of the individual dislocation boundaries in the cell walls produce changes in relative cell-to-cell misorientation. At higher temperatures, cell wall migration and resultant growth occurs. This work has been completed and is now being incorporated as part of the doctoral dissertation of N. Ramchandran.

## B. Oxidation of Oxide Containing Alloys

The use of hot stage electron microscopy affords the opportunity to study in situ, the oxidation behavior of metal alloys. In particular, the influence of a distributed oxide phase on the subsequent nucleation and growth of oxide films can be followed in detail. Thin film specimens of Al-Al<sub>2</sub>O<sub>3</sub> SAP-type alloys have been oxidized in the electron microscope at partial pressures of oxygen of approximately 10<sup>-5</sup> torr in the temperature range of from 300 to 600° C. The oxide growth on the aluminum matrix at lower temperatures occurs rather slowly. The interface is impeded by the presence of second phase Al<sub>2</sub>O<sub>3</sub> particles where such particles extend through the foil surface. This impeding effect is probably due to beam and column contamination around these surface particles acting as a mechanical barrier to oxygen. Electron diffraction studies of the oxide structure indicate that the aluminum oxide formed at the lower temperature is of a type not previously reported. At higher temperatures, within the previously formed oxide film, a higher crystalline form of aluminum oxide nucleates and grows. This oxide is probably Al<sub>2</sub>O<sub>3</sub>, the same oxide phase intentionally present in the alloy. It has been noted that the Al<sub>2</sub>O<sub>3</sub> in the SAP alloy can, but need not, act as the nucleation site for this oxide formation. Interestingly, this oxide formation is reversible in the microscope indicating that these observations are being made under close to equilibrium conditions. This program is almost complete.

## C. Work Hardening Behavior in Precipitation-Hardened Alloys

The role of the interface structure upon dislocation distributed phase interactions, appears upon the basis of theoretical considerations, to be of prime importance in the development of substructure during deformation. The substructural development in an Al-Ag precipitation-hardened alloy has been followed by means of transmission electron microscopy.

In this alloy, studies of the two phase structure have centered upon aging treatments which produce the  $\gamma'$  precipitate. This phase forms as platelets within the alloy matrix dividing the structure into blocks. Deformation in this system produces three stages of substructure development. Initially, the precipitate-matrix interfaces act as dislocation sources and sink so as to provide no increase of substructure. Instead, each precipitate-bounded matrix block deforms rather uniformly as an entity producing block to block misorientations. This can be followed rather neatly by moiré fringing appearing as a result of matrix to precipitate plate rotations, in effect, a type of microstrain gage. In this deformation range no increase in flow stress for the alloy occurs. At higher deformations, dislocation motion is no longer contained within a matrix block, and particle shear coupled with increases in substructure occurs. As soon as this substructural change happens, the flow stress of the alloy increases by approximately 50%. At very high deformations, dynamic recovery occurs, evidenced by symmetric tangle formation. This work has been completed and is currently being prepared for publication. This material will be incorporated in the doctoral dissertation of C. Barton.

#### D. Fracture Behavior

The influence of a distributed phase upon fracture mode and crack propagation is being studied in steel. Replication studies of the fracture surfaces of these alloys broken in fatigue, are being used to establish the mechanism by which dissolved gasses, particularly hydrogen, affect fatigue fracture. This program is currently in progress and is being handled in cooperation with Dr. H. Rogers of the G. E. Research Laboratory.

#### E. Precipitation Kinetics

The formation of quench and solute induced defect formation apparently control the nucleation and growth kinetics of many precipitate phases. In the studies of the Al-Ag system, several observations were made of such nucleation behavior. Currently, this area is being pursued, with the emphasis on the formation of the defect structure.

#### F. Martensite Transformation

The kinetics of the martensite transformation in the Fe-C system have proved elusive. As a result of recent work in this laboratory, it is felt that this transformation may be controlled by the shear strength of austenite. For this reason an investigation of the kinetics of the martensite transformation as a function of austenite strength has been undertaken. This program is currently in progress.

#### G. Theoretical Studies

Theoretical studies of dispersion-strengthening based upon dislocation theory are progressing on a continuing basis.

### Mechanisms of Solidification

470.10

Senior Investigator:	W.J. Childs, Ph.D. Professor of Metallurgical Engineering
Research Staff:	J.J. Frawley, M. Met. E. Graduate Assistant

Studies of vibrational effects on nucleation of supercooled metals were extended to the 20 kilocycle range. An accoustical horn was designed to couple a ceramic transducer to a small Pyrex crucible which was held in a 7/8" diameter hole machined in the end of the horn. A silicone oil was used to improve coupling between the horn and the crucible.

As the ultrasonic energy was increased, a point was reached at which cavitation occurred. The supercooling obtained under these conditions was approximately  $10^{\circ}\text{C}$  as contrasted to about  $60^{\circ}\text{C}$  supercooling without vibration. Additional energy above that required for cavitation did not cause any further decrease in supercooling for nucleation. High speed movies were made to substantiate the existence of cavitation.

These results were qualitatively different from the behavior at vibrational frequencies of 15 to 64 cps where the dynamic supercooling varied continuously with the applied energy. This was probably true since there was no evidence of cavitation.

Work was started on measuring the electrical resistance of bismuth as a function of the amount of supercooling in order to explore the structure of the supercooled state.

#### Ultrasonic Research

470.11

Senior Investigator: H.B. Huntington, Ph.D.  
Professor of Physics

Research Staff: V. Tinto, M.S.  
Graduate Assistant  
J.H. Zablotney, B.S.  
Graduate Assistant

The work on the third order elastic constants of alkali halides, reported last time for NaCl and KCl, has been extended to LiF. The results give four independent relations and two internal checks. The latter were quite satisfactory. Cross checking with the hydrostatic measurements of Miller gave three additional checks that were validated to within 12% or better, and an additional independent relation. Because of the known deviation from the Cauchy relations for the second order elastic constants in LiF, no attempt was made to invoke these relations in the third order--as we did for NaCl and KCl. Publication of these results will be delayed pending the consideration of a model for LiF involving non-central forces.

We have begun an investigation of ultrasonic beam interactions using two high power Arenberg oscillators. The initial experiments will be mixing 5 and 25 Mc/s beams in an aluminum disk and trying to pick up 30 Mc/s. We have shown that it is practical to use plano-concave "lenses" of aluminum to take beams in or out of the disk at arbitrary angles through a thin oil or grease films.

#### Ultrasonic Pulse Interferometry

470.12

Senior Investigator: S. Katz, Ph.D.  
Professor of Geology

Research Staff:

R.N. Schock, M.S.  
Graduate Assistant

During the past six months the study of the effect of pressure and temperature on solid inorganic compounds has continued. The pressure cell utilizes diamond anvils and permits visual microscopic, infrared spectrophotometric, and x-ray examination. The system  $\text{CaCO}_3$  is of primary concern, but  $\text{AgI}$  was found, during use as a pressure calibrant, to have several interesting and unreported properties, which are being further investigated.

$\text{AgI}$  is found to dissociate at an internal pressure of approximately 4 kb at room temperature. The dissociation rate increases with temperature. Under the influence of the radial pressure gradient imposed across the sample by the geometry of the pressure cell,  $\text{I}_2$  formed as a result of this dissociation is observed to migrate toward the central, high-pressure area of the cell. At the same time, free  $\text{Ag}$  is observed in the low-pressure phases of  $\text{AgI}$ . It may be possible to account for this migration on the basis of the pressure-dependence of compressibility of  $\text{AgI}$  relative to its constituents  $\text{Ag}$  and  $\text{I}_2$ . This effect may be analogous to the Soret effect, in which the constituents of an alloy can migrate either with or against a thermal gradient, depending upon the particular material and its properties. Electrical conductivity measurements have been made in a larger pressure device to 50 kb, using tungsten-carbide anvils. The results of these measurements tend to confirm the optical studies of  $\text{AgI}$ .

Continuing studies on calcite ( $\text{CaCO}_3$ ) and its polymorph, aragonite, using infrared absorption techniques, indicate that in the diamond-anvil apparatus aragonite is formed by two mechanisms: an instantaneous transformation upon the application of pressure, possibly associated with the large shear stress in this pressure cell; then a progressive increase in aragonite, at an exponential rate typical of rate-sensitive processes. Calculations using data at  $100^\circ \text{C}$  and 27 kb give an order of reaction of approximately 18 and a reaction rate constant for 100 % completion of  $10^{-14}$  percent/min.

A summary article of high pressure research in geophysics was completed and submitted for publication.

It is expected that these studies of the optical and electrical properties of  $\text{AgI}$  and of the kinetics of the calcite  $\rightleftharpoons$  aragonite reaction will be completed during the next reporting period.

The Relation of Molecular Structure and Intermolecular 470.15  
Action in Flow of Polymers and Polymer Dispersions  
as a Function of Temperature and Shear Rate

Senior Investigator:

W.H. Bauer, Ph.D.  
Professor of Physical Chemistry

Research Staff:

W. Boyce, Ph.D.  
Graduate Assistant



The objective of the work being conducted is to study the physical properties, such as molecular weight, flow properties and molecular weight distribution of polybutadiene polymers of the type used in the preparation of solid propellants.

A study has been made of the flow properties of a series of polybutadiene polymers at several temperatures and a number of shear rates correlating capillary and rotary viscometric data. This work is being reported in the thesis of William Boyce and is now in preparation.

Future work involves the study of the molecular weight distribution of these polymers making use of gel permeation methods and study of the flow properties of concentrated solutions of polybutadienes.

#### High Temperature and Mechanical Metallurgy 470.18

Senior Investigator: W.R. Clough, Sc.D.  
Associate Professor of  
Metallurgical Engineering

Research Staff: L.A. Jackman, B.Met.E.  
Research Fellow

This research is directed towards determining the rate-controlling mechanisms operating during the low temperature (-196 to 200 degrees centigrade), thermally activated deformation of BCC and FCC solid solutions. Emphasis has been placed on BCC solid solutions because the results should greatly aid in revealing the controversial mechanism controlling the thermally activated deformation of pure BCC metals. The approach that is being pursued consists of utilizing a constant stress creep machine to determine activation energies, activation volumes, and pre-exponential terms in the deformation rate equation over a range of temperatures, applied stresses, effective stresses, and strain rates.

The design and construction of a constant stress creep machine has been completed. Also, it has been necessary to build a constant temperature bath for use on an Instron tensile machine in order to determine the effective stress. Transient creep experiments are presently being performed on Cb - Ta alloys. This alloy system has been chosen to isolate the effect of the shear modulus.

Other alloys which have been obtained and will be tested in the near future include alloys in the Cb - V, Ni - Pt, and Ni - Pd alloy systems.

#### Low Temperature Physics 470.19

Senior Investigator: R.W. Shaw, Ph.D.  
Associate Professor of Physics

**Research Staff:**

W.A. Fate, B.S.  
 Graduate Assistant  
 G.I. Kaufman, B.S.  
 Graduate Assistant  
 C.P. Newcomb, B.S.  
 Graduate Assistant  
 J.F. Schenck, Ph.D.  
 Graduate Assistant  
 J.S. Willis, M.S.  
 Graduate Assistant  
 D.S. Woo, B.S.  
 Graduate Assistant

Considerable time and effort during the subject period has gone into moving to and setting up in the new Materials Research Center. These much improved quarters will make possible more effective operation in the future. In the research areas supported in part by this contract the following progress has been made:

**A. Ultrasonic Attenuation in Superconductors**

The amplitude dependence of the ultrasonic attenuation in superconducting lead, first observed here, is being further investigated in the light of a theory proposed by W.P. Mason and described in the previous report. Specially, the temperature dependence of the effect appears to deviate considerably from his predictions. The cause of these deviations is being pursued here both experimentally and theoretically and, we believe, is basically understood.

Work is progressing on ultrasonic studies in superconducting mercury and thallium.

**B. Superconductivity and Lattice Defects**

The results and implications of studies on the effects of lattice defects in pure and alloy superconductors are being applied to construct a theoretical model. This appears to explain the existing observations and will be used to make predictions for further experiments. The basis of the model is that defects, particularly dislocations, collect in local regions which therefore have quite different electronic properties (mean free path, etc.) than the surroundings. These regions have a higher Ginsburg-Landau parameter,  $K$ , and this can lead to the resistance minimum in alloys, broadened resistive transitions, and hysteresis and trapped flux in magnetic moment measurements.

**Dispersion-Strengthened Materials**

470.23

**Senior Investigator:**

F.V. Lenel, Ph.D.  
 Professor of Metallurgical Engineering

**Research Staff:**

G. Leverant, B.S.  
Research Fellow  
J. Hirschhorn, M.S.  
Research Fellow  
H. Nayer, MS.  
Graduate Assistant  
M. Singh, B.Sc.  
Graduate Assistant

Mr. Hirschhorn completed his work on the structure of internally oxidized silver alloys and submitted a thesis to the Department of Materials Engineering, which was accepted. On the basis of his hardness, lattice parameter, electron microscopic and electron diffraction measurement, Mr. Hirschhorn developed a theory of dispersion strengthening in these alloys. Since the direct observations by electron microscopy were very difficult and the result of these observations quite sketchy, the theory must be considered tentative rather than definitive.

Good progress is being made in the determination of the creep properties of dispersion strengthened silver-magnesium alloys and the comparison of creep in pure silver and these alloys. Data on both the stress and the temperature dependence of the steady state creep rates are obtained.

Mr. Singh completed a master's thesis on the plastic deformation of internally oxidized silver-magnesium single crystals. His results may be summarized as follows:

1. The critical resolved shear stress for internally oxidized Ag-Mg single crystal increases from 4150 P.S.I. for 0.3 atomic % Mg to 13,137 P.S.I. for 1.07 atomic % Mg for the same oxidation temperature of 900°C. That is, increasing solute content increases the C.R.S.S. at particular oxidation temperatures.
2. For the same amount of solute content (1.06 atomic % Mg), the C.R.S.S. for the alloy oxidized at 900°C is 11,914 P.S.I., and for the one oxidized at 600°C is 20,960 P.S.I. Thus the C.R.S.S. increases with decreasing oxidation temperature.
3. The effect on internal oxidation is to inhibit the plastic deformation by slip but not by twinning. This is evidenced by the findings that at low alloy contents the mechanism of plastic deformation is by slip, but at higher alloy content the preferred mode of deformation is by twinning, depending on the initial orientation of the crystal. It has been observed that the twinning occurs only after the crystal has work hardened to the stress level where twinning can occur.

Creep specimens of ice strengthened with a fine dispersion of silica are being successfully tested in creep at temperatures between -25 and -10°C. Their creep strength is considerably higher than that

of pure ice. Quantitative data on the creep rate of dispersion-strengthened ice as a function of silica content, temperature and applied stress are being obtained. A fixture to determine the tensile strength of dispersion strengthened ice is being built.

#### Mettalic Dissolution

470.25

Senior Investigator: N.D. Greene, Ph.D.  
Professor Metallurgical Engineering

Research Staff: H. Cleary, B.S.  
Graduate Assistant

The purpose of this program is to determine the basic corrosion and electrochemical characteristics of iron and iron alloys (steels). Composition and/or metallurgical structure have a pronounced effect on chemical behavior as evidenced by the wide variations observed between nearly identical samples.

Over 70 plain carbon and low alloy steels, in addition to several grades of zone refined iron have been obtained for testing. Corrosion testing of these materials is in progress. A 30-fold difference in corrosion rate has been observed for two plain carbon steels in IN sulfuric acid. Additional tests are being carried out using 0.1N sulfuric acid and 0.1M citric acid.

#### Nuclear Magnetic Resonance Research

470.26

Senior Investigator: P.A. Casabella, Ph.D.  
Associate Professor of Physics

Research Staff: J.L. Marsh, Jr., M.S.  
Research Assistant  
C.J. Miller, B.S.  
Graduate Assistant

The measurement of the quadrupole anti-shielding effects of ion cores in alkali halide crystals is progressing satisfactorily. Both the  $\text{Na}^{23}$  and  $\text{Cl}^{35}$  nuclear magnetic resonances in single crystals of sodium chloride have broadened measurably under a uniaxial compression. This broadening has been used to deduce the electric field gradient induced by the compression at the sites of the nuclei studied. The electric field gradient expected from the compression is now being calculated. When this calculation is complete a comparison of the results with the experimental results will yield the anti-shielding factors of the ion cores. Meanwhile a similar experiment has been started on sodium bromide.

X-Ray Scattering

470.28

Senior Investigator: J.L. Katz, Ph.D.  
Associate Professor of Physics

Research Staff: S. Raman, Ph.D.  
Assistant Professor of Physics  
R. Ramachandran  
Student Assistant

The present research program has been concerned with two main areas: 1) studies of the crystal and molecular structure of the coordination compounds of the platinum group metals and 2) lattice dynamic studies of certain metals and alloys.

In the former area, a completed study on "The Crystal and Molecular Structure of Ruthenium-Sulfur Dioxide Coordination Compounds I, Chlorotetraamine (sulfur dioxide) - ruthenium (II) Chloride" by Lester H. Vogt, Jr., J. Lawrence Katz, and Stephen E. Wiberley appeared in *Inorganic Chemistry*, 4, 1157 (1965). A similar study of the isomorphous bromo bromide structure is now in progress.

Recently completed in the latter area has been a study on "Measurements of X-Ray Debye Temperature of Pure Nickel and Chromium at Thermal Temperatures Ranging from 100° to 500° K," by Ronald H. Wilson, Earl F. Skelton and J. Lawrence Katz which is being submitted to the *Journal of the Physics and Chemistry of Solids*. A liquid helium cryostat for performing these x-ray studies down to approximately 3.5° K will be delivered in September. In addition to continuing the measurements on nickel and chromium down to these temperatures, several new metals including, zinc and gold are being studied.

Thermal Properties of Polymers

470.29

Senior Investigator: D. Hansen, Ph.D.  
Associate Professor of Chemical  
Engineering

Research Staff: B. Washo, B.S.  
National Defense Education Act Fellow  
N. Watkins, B.S.  
Graduate Assistant  
R. Crystal, B.Ch.E.  
Graduate Assistant

A. Thermal Conductivity

Measurements of the thermal conductivity anisotropy in oriented polymers are being continued. These are long duration experiments but it is expected that sufficient data may be gathered in the next six months to permit some preliminary conclusions.

Theoretical calculations which predict that thermal conductivity of an amorphous polymer should increase with molecular weight, decrease with degree of branching, and increase with degree of cross-linking have been compared with available data. In general the data support the calculations. A detailed report on this comparison has been submitted for publication.

#### B. Structure

The size and arrangement of crystallites in polymers, such as in spherulite patterns, is an important determining factor in the properties of crystalline polymers. By a detailed sequence of optical and electron microscope observations on thin sections cut from polymers crystallized under controlled conditions, this study should aid in understanding the three-dimensional arrangements of crystallites and the relation of these arrangements to crystallization conditions. Observations are now being made on polyethyleneterephthalate and polyethylene.

#### Glass and Non-Metallic Materials

470.30

Senior Investigator: J.D. Mackenzie, Ph.D.  
Professor of Materials Science

Research Staff: R. Hakim, B.S.  
Graduate Assistant  
W. Frey, B.S.  
Graduate Assistant  
R. Mehalso, B.S.  
Graduate Assistant  
D. Secrist, B.S.  
Graduate Assistant

The objectives of this work are twofold: (a) to correlate structures and properties of glasses and other non-metallic solids, and (b) to prepare new non-metallic materials and study their properties.

During this period, research has been carried out on (1) semi-conducting glasses (2) ceramic-metal interfaces, (3) glass-crystalline oxide composite materials, (4) electrical conduction in high resistivity glasses and (5) vapor deposition of oxide glasses. These projects are being continued.

#### Vibrational Spectroscopy Inorganic Substances in the Vapor Phase

470.31

Senior Investigator: S.C. Wait, Jr., Ph.D.  
Associate Professor Physical Chemistry

Research Staff:

G. Kelly, B.A.  
Graduate Assistant

Investigations of inorganic nitrates in the vapor phase are being undertaken for the purpose of making vibrational analyses and studying ionic interactions at high temperatures. Attempts to obtain spectra of potassium nitrate at 600°C. on a Perkin-Elmer Model 421 infrared spectrophotometer have yielded some results. Peaks in the 2300-2400 region, which appear weak in the solid, and in the 1450  $\text{cm}^{-1}$  region have been observed. In the last run, a band due to NO appeared, thereby indicating some decomposition of the nitrate ion at these temperatures. Further efforts are directed towards obtaining better spectra for potassium nitrate and other alkali metal nitrates.

Irreversible Thermodynamics of the Solid 470.32  
State of Linear High Polymers

Senior Investigator:

B. Wunderlich, Ph.D.  
Professor of Chemistry

Research Staff:

E. Hellmuth, Ph.D.  
Research Associate  
P.K. Sullivan, Ph.D. (Fall 1965)  
Graduate Assistant  
J.M. Rankin  
Graduate Assistant  
S. Wolpert  
Graduate Assistant

Extended chain equilibrium crystals of polymers are available by crystallization under elevated pressure and by direct crystallization from the monomer.

During the past six months, the superheating studies on polyethylene, polymethylene and polytetrafluoroethylene have been completed. This phase of research has come to a temporary halt with the leaving of Dr. Hellmuth (now Assistant Professor at the University of Missouri at Kansas City) and Mr. J.M. Rankin, B.S., RPI, 1965 (now graduate assistant of Dr. Hellmuth).

Dr. P.K. Sullivan left the project after completion of his Ph.D. thesis in July, 1965, to accept a research position at the National Bureau of Standards. Out of his work grew a new research project, namely the study of the dissolution temperature of the equilibrium crystals of polyethylene in not crystallized polyethylenes of different molecular weights and possibly also copolymers of polyethylene. This work will be continued in the next six months by the senior investigator.

A study of the seeding of polyethylene melts with equilibrium crystals has begun by the senior investigator during the last six months and is hoped to be concluded shortly.

S. Wolpert has started a major investigation of the time dependence of glass transitions of polymers and monomers using the previously purchased DTA apparatus vacated by Dr. E. Hellmuth.

Ultra-Low Temperature Solid State Physics Research 470.33

Senior Investigator: G.L. Salinger, Ph.D.  
Assistant Professor of Physics

Research Staff: Y.C. Chiang, M.S.  
Graduate Assistant  
C.L. Choy, B.S.  
Graduate Assistant

The object of this program is to measure thermal properties of magnetic salts at low temperatures. In particular, the thermal conductivity of magnetic insulators will be measured at temperatures well below their magnetic transition temperature, in order to investigate the interaction in the magnetic system. Similar measurements above the transition temperature can, under favorable circumstances, give information about the interaction of lattice waves.

The past six months have been spent in the design and construction of the cryostat. A vibration free mount has been built. The gas handling and vacuum systems for both  $\text{He}^3$  and  $\text{He}^4$  are almost finished.

In the next six months it is hoped that the cryostat will be completed and tested and that the experimental crystals will be grown.

Thermal Decomposition of Inorganic 470.34  
Coordination Compounds

Senior Investigator: R.A. Bailey, Ph.D.  
Assistant Professor of Physics

Research Staff: F. Montillo, M.S.  
Graduate Assistant  
W. Tangredi, M.S.  
Graduate Assistant

The objective of this project is to study the thermal decomposition of coordination complexes involving organic ligands. Of primary interest is the manner in which these compounds decompose; consequently the identities of the products and their relative yields are under investigation. This is in contrast to many studies which are concerned only with the conditions under which decomposition takes place.

Work has been carried out on the urea complexes of several metals (primarily copper, zinc, and cadmium at this point). Thermogravimetric studies have been made on these, and the products formed at each distinct phase of the decomposition process investigated. Identification of both gaseous and solid products is generally by infrared spectroscopy, although other techniques are used when appropriate.



Results indicate that the stability of the compound and the form of decomposition can be influenced strongly by the nature of the metal ion. In some cases, in air, decomposition of the urea occurs with part of the residue remaining attached to the metal, while in others complete oxidation occurs. The complete study of the decomposition products has not yet been completed.

Further work will involve the completion of these studies in air, and their extension to vacuum and inert atmosphere conditions.

Thermodynamics and Kinetics Vaporization      470.35  
Processes for Inorganic Materials

Senior Investigator:      H. Wiedemeier, Ph.D.  
Assistant Professor of Chemistry

Research Staff:      G. Sigai,  
Undergraduate Assistant

The objectives of the present research project include the investigation of the thermodynamics and kinetic properties of transition metal and group VI compounds upon vaporization at elevated temperatures.

Special transport furnaces for the preparation of single crystals have been constructed. Test runs have been carried out successfully. A high vacuum system for loading and sealing transport tubes is built and in operation now.

Samples of manganese sulfides and selenides have been obtained in single and polycrystalline form.

Techniques are being developed to produce single crystals of larger sizes and ultrahigh purities.

Spectroscopic Studies of Synthetic Reversible      470.36  
Oxygen-Carrying Chelates

Senior Investigator:      S.E. Wiberley, Ph.D.  
Professor of Chemistry

Research Staff:      T. Comfort, M.S.  
Graduate Assistant  
G. Merrill

Efforts to prepare solid iron (II) bis dimethylgloxime have been continued. The procedure of Tschugaeff for preparing the octahedral complex of  $\text{Fe}(\text{DM})_2 \cdot 2\text{X}$  where X is a monodentate base ligand (either

ammonia or pyridine) and DM is dimethylgloxime has been followed. However, attempts to remove the base molecules by heating the compounds in vacuo have been unsuccessful. A transitory purple red complex is formed in the reaction between ferrous sulfate and dimethylgloxime in ammonical solution. This complex is believed to be  $\text{Fe (DM)}_2 \cdot 2\text{NH}_3$ . Upon standing the complex turns brown. At dry ice bath temperatures the purple red complex can be kept stable for days. However, a solid material can not be isolated by crystallization. Experiments to produce iron (II) bis dimethylgloxime by heating anhydrous ferrous sulfate and dimethylgloxime at elevated temperatures in an inert atmosphere were unsuccessful.

#### Electron Spin Resonance

470.37

Senior Investigator: A.C. Greene, Ph.D.  
Assistant Professor of Physics

Research Staff: D.D. Moyle, B.S.  
Graduate Assistant  
D.B. Williams, B.S.  
Graduate Assistant

An electron spin resonance program has been initiated with the design and construction of a versatile spectrometer system. At the present time the X-band homodyne spectrometer is operated as a balanced mixer type with either crystal or bolometer detection. The microwave cavity system allows experiments to be conducted from 77°K to 500°K with either liquid or solid sample specimens. Under construction are an electron-nucleus double resonance system, using a slow wave helix, and compatible liquid helium temperature apparatus. The system is being used primarily for studies of radiation effects and defect-defect interactions in solids but will also be available as a supplement to various interdisciplinary programs within the Institute.

#### Polymer Characterization

470.38

Senior Investigator: F.W. Billmeyer, Jr., Ph.D.  
Professor of Analytical Chemistry

Research Staff: N.K. Blackwood, B.S.  
Graduate Assistant

Research on the principles of color technology has been initiated with the purchase, in part through this project, of a General Electric Recording Spectrophotometer, the referee instrument for precise and accurate color measurement. The overall objective of the research involving this instrument is to improve the precision and accuracy of color measurement as practiced in industry. It is estimated that an improvement of at least one order of magnitude can be realized over

the present state of industrial practice, as exemplified by the senior investigator's previous studies.<sup>1</sup>

Specific objectives envisioned for this project are the following:

1. Development of highly precise photometric measurement techniques, their application in the establishment of suitable primary standards of transmittance, and the use of these standards to calibrate the photometric scale of the G. E. spectrophotometer and other color measuring instruments.

2. Development of techniques for the multi-point calibration of the wavelength scale of relatively broad band-pass instruments such as the G. E. spectrophotometer, and implementation of their application to field calibration of such instruments.

3. Development of novel white reflectance standards of improved durability, reproducibility, and spectrally non-selective character, and the development and application of techniques for their accurate calibration in terms of the reflectance of the perfect diffuser.

Preliminary studies during the short period following the delivery of the instrument have been directed towards assessing its performance compared to industry standards and towards testing improved procedures for its calibration and reproducible operation, prior to the application of the novel techniques making up the objectives of the research.

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<sup>1</sup>F.W. Billmeyer, Jr., J. Opt. Soc. Am., 55, 707 (1965).

TECHNICAL PAPERS SUBMITTED FOR PUBLICATION

Hellmuth, E., Wunderlich, B.

"Superheating of Linear High Polymer Crystals"

Submitted to Journal of Applied Physics

Arakawa, T., Wunderlich, B.

"Thermodynamic Properties of Extended Chain Polymethylene Single Crystals"

Submitted to Journal of Polymer Science

Chang, Z.P.

"The Third Order Elastic Constants of NaCl and KCl

Single Crystals"

Submitted to Journal of Physical Review

Wunderlich, B., Hellmuth, E.

"Superheating Studies on Polymer Crystals"

Presented at "First International Thermal Analysis Conference" held in Aberdeen, Scotland on September 6 - 9, 1965. Published in the proceedings of that meeting.

Lang, F.T., Strong, R.L.

"Gas Phase Molecular Complexes. The Diethyl Ether-Iodine and Benzene-Iodine Charge-Transfer Complexes"

Submitted to Journal of American Chemical Society

Hansen, D., Kantayya, R.C., Ho, C.C.

"Thermal Conductivity of High Polymers - The Influence of Molecular Weight"

Submitted to Society of Plastics Engineers

Hellmuth, E., Wunderlich, B., Ranken, J.M., Jr.

"Superheating of Linear High Polymers. Polytetrafluoroethylene"

Submitted to Journal of Applied Polymer Science

## APPENDIX A

### Members of Interdisciplinary Materials Research Center Faculty Committee

S.E. Wiberley, Chairman	Professor of Analytical Chemistry and Dean of the Graduate School
G.S. Ansell	Professor of Metallurgical Engineering
W.H. Bauer	Professor of Physical Chemistry and Dean of the School of Science
A.A. Burr	Professor of Metallurgical Engineering and Dean of the School of Engineering
E.F. Nippes	Director of the Research Division
H.B. Huntington	Professor of Physics, Chairman of the Department of Physics
G.J. Janz	Professor of Physical Chemistry Chairman of the Department of Chemistry
F.V. Lenel	Professor of Metallurgical Engineering
S.S. Sternstein	Associate Professor of Chemical Engineering
J.M. LoGiudice	Administrative Director of the Interdisciplinary Materials Research Center